



Short communication

A safe and high-rate negative electrode for sodium-ion batteries: Hard carbon in NaFSA- $C_1C_3$ pyrFSA ionic liquid at 363 K



Atsushi Fukunaga <sup>a,b</sup>, Toshiyuki Nohira <sup>a,\*</sup>, Rika Hagiwara <sup>a,\*</sup>, Koma Numata <sup>b</sup>, Eiko Itani <sup>b</sup>, Shoichiro Sakai <sup>b</sup>, Koji Nitta <sup>b</sup>, Shinji Inazawa <sup>b</sup>

<sup>a</sup>Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

<sup>b</sup>Sumitomo Electric Industries Ltd., 1-1-3 Shimaya, Konohana-ku, Osaka 554-0024, Japan

HIGHLIGHTS

- Hard carbon (HC) negative electrodes were examined in several ionic liquids.
- A Na/NaFSA- $C_1C_3$ pyrFSA/HC cell exhibited good cycle performance at 363 K.
- The discharge capacity was 260 mAh (g-HC)<sup>-1</sup> at 50 mA (g-HC)<sup>-1</sup>.
- The cell showed high rate capability up to 1000 mA (g-HC)<sup>-1</sup>.
- The coulombic efficiency was higher than 99.9% for 40 cycles.

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ABSTRACT

Charge-discharge properties of hard carbon (HC) for sodium secondary batteries using NaFSA- $C_1C_3$ pyrFSA (FSA: bis(fluorosulfonyl)amide,  $C_1C_3$ pyr: *N*-methyl-*N*-propylpyrrolidinium) ionic liquids were investigated. A Na/NaFSA- $C_1C_3$ FSA/HC cell showed reversible capacity of 260 mAh (g-HC)<sup>-1</sup> at a constant rate of 50 mA (g-HC)<sup>-1</sup> at 363 K, maintaining cell capacities of approximately 95.5% of the initial capacity after 50 cycles. Coulombic efficiency was higher than 99.5% except for the initial few cycles, reaching 99.9% after 40 cycles. The Na/NaFSA- $C_1C_3$ pyrFSA/HC cell also exhibited a high rate capability of 211 mAh (g-HC)<sup>-1</sup> at a rate of 1000 mA (g-HC)<sup>-1</sup>, which corresponds to a charge rate of approximately 4C.

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## 1. Introduction

The demand for secondary batteries for energy-storage devices has recently experienced significant growth for use in important applications such as load leveling, emergency power supply devices, and smart grids. As high-performance secondary batteries, lithium-ion batteries (LIB) are highly popular not only for mobile applications but also for electric vehicle and household uses. However, difficulties in locating and extracting material resources for LIBs are anticipated in the near future, because such devices

employ minor metals like cobalt and nickel. Even for lithium, it is difficult to maintain a stable supply because high-quality lithium resources are unevenly distributed, which occur mainly in China and South America. Thus, the research and development of secondary batteries using only easily available raw materials such as sodium has become an active field of investigation in recent times. In particular, the number of reports on sodium secondary batteries has risen rapidly in the past 2–3 years [1–8]. Sodium, which can be easily obtained from seawater or the earth's crust, possesses a reasonably negative standard redox potential of  $-2.714$  V vs. SHE. Furthermore, many advanced technologies designed for use in LIBs are expected to be applicable for sodium secondary batteries.

The development of sodium secondary batteries has a long history; batteries using a  $\beta''$ -alumina electrolyte have been studied for many years [9–12], and Na/S and Na/NiCl<sub>2</sub> batteries are

\* Corresponding authors. Tel.: +81 75 753 5827; fax: +81 75 753 5906.

E-mail addresses: [nohira@energy.kyoto-u.ac.jp](mailto:nohira@energy.kyoto-u.ac.jp) (T. Nohira), [hagiwara@energy.kyoto-u.ac.jp](mailto:hagiwara@energy.kyoto-u.ac.jp) (R. Hagiwara).

currently in practical usage as large-scale energy-storage devices for mega solar power plants and wind farms. However, these batteries have less-than-ideal operating conditions for practical industrial applications. The  $\beta''$ -alumina electrolyte needs high operation temperatures of approximately 573 K to raise its conductivity. Furthermore, Na/S and Na/NiCl<sub>2</sub> batteries require liquid sodium metal, which is an extremely hazardous material. Thus, storage and installation of Na/S and Na/NiCl<sub>2</sub> batteries have been restricted because of their large sizes and regulations placed on the use of sodium metal.

At the same time, reports on sodium secondary batteries using organic electrolytes have recently increased [1–8]. These reports highlight promising advantages of the electrolyte, such as energy density, cost, and material abundance. However, the use of organic solvents in batteries, similar to conventional LIBs, requires considerations for safety apparatus, because manufacturing hazards can prove destructive (and potentially lethal) for production of large-scale batteries. Moreover, the required organic solvents cannot be used at intermediate or high temperatures because of their high volatilities. Accordingly, large-scale and assembled sodium secondary batteries using organic solvents have to be equipped with cooling systems similar to LIBs in order to assure the safety.

To address the drawbacks listed above, the development of safe and high-performance electrolytes is strongly needed. We have developed several ionic liquids [13] that have high thermal stabilities, high ionic conductivities, and wide electrochemical windows as electrolytes for sodium secondary batteries and demonstrated their actual operation: Na/NaTFSA-CsTFSA/NaCrO<sub>2</sub> (TFSA: bis(trifluoromethylsulfonyl)amide; operating temperature: 423 K) [14], and Na/NaFSA-KFSA/NaCrO<sub>2</sub> (FSA: bis(fluorosulfonyl)amide; operating temperature: 353 K) [15,16]. We have confirmed excellent cycle performances, rate capabilities, and wide operating temperatures for the batteries using these ionic liquids as the electrolyte medium. In these studies, sodium metal was used as a negative electrode. Dendrite formation as a result of the deposition of sodium metal can be suppressed by operations at elevated temperatures, close to the melting point of sodium. However, the dendritic deposition of sodium metal is difficult to prevent completely and is unavoidable, especially at lower operation temperatures. To avoid the use of Na metal, we also investigated negative electrodes composed of Sn–Na alloys [17,18]. Although the electrode showed a very high capacity of more than 700 mAh (g-Sn)<sup>-1</sup>, its cyclability was limited because of the volume change during alloying and dealloying processes.

Concerning the studies on negative electrodes in organic electrolytes, Komaba et al. [19] and Ponrouche et al. [20] have reported that hard carbon (HC) shows a stable charge–discharge behavior with 250–300 mAh (g-HC)<sup>-1</sup> at 298 K. However, HC shows poor rate capability at room temperature; the capacity at a discharge rate of 2C shows only 40% of the capacity at rate of C/10 [20]. Because high rate capability is one of the more important properties for the practical use of HC (e.g. batteries for EVs), the improvement of rate capability is necessary for the Na/HC system.

It is reasonably expected that rate capability is largely improved by the elevation of operation temperature. We have already reported an excellent rate capability of 2000 mA (g-NaCrO<sub>2</sub>)<sup>-1</sup> (approximately 18C) for the NaCrO<sub>2</sub> positive electrode in a NaFSA-KFSA ionic liquid at 353 K [16]. Thus, we first tried applying the HC negative electrode to NaFSA-KFSA ionic liquid at 363 K. As described in Section 3, however, a Na/NaFSA-KFSA/HC cell showed a small discharge capacity and poor cyclability. Because the presence of K<sup>+</sup> ions was presumed to be the cause of the poor properties obtained, we selected NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA (C<sub>1</sub>C<sub>3</sub>pyr: N-methyl-N-propylpyrrolidinium, Fig. 1) as a second ionic liquid for

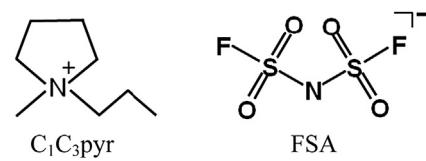


Fig. 1. Structure formula of C<sub>1</sub>C<sub>3</sub>pyrFSA.

investigation. In our previous study, fundamental properties such as ionic conductivity and viscosity were measured for this ionic liquid; a Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA (20:80 mol%)/NaCrO<sub>2</sub> cell was successfully operated at 298–353 K [21]. In the present study, we report the charge–discharge behavior of Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA (10:90 mol%)/HC cells at 363 K. To study the influence of the K<sup>+</sup> ion, the behavior of the HC negative electrode was also investigated by using different compositions of ionic liquids (NaFSA:KFSA:C<sub>1</sub>C<sub>3</sub>pyrFSA = 8:2:90, 5:5:90, 0:10:90 mol%). Finally, to demonstrate high rate capability at 363 K, the Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cell was tested in the range 25–1000 mA (g-HC)<sup>-1</sup>.

## 2. Experimental

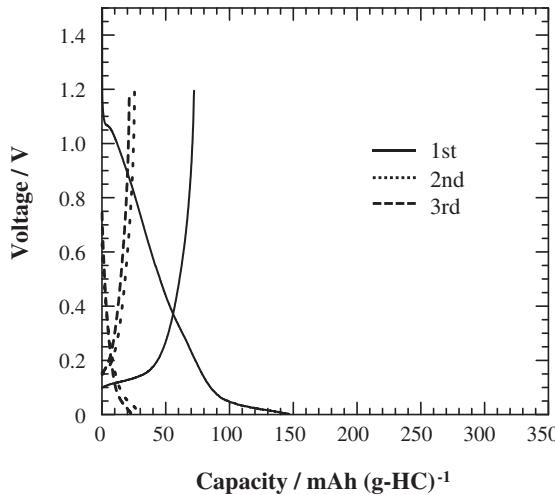
NaFSA, KFSA (Mitsubishi Materials Electronic Chemicals Co., Ltd., Japan, >99.0%) and C<sub>1</sub>C<sub>3</sub>pyrFSA (Kanto Chemical Co., Inc. Japan, >99.0%) were dried under vacuum at 333 K for 24 h. The eutectic NaFSA-KFSA ionic liquid (NaFSA:KFSA = 56:44 mol% [15]) was prepared by grinding the two salts with a mortar and pestle. NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA ionic liquid (NaFSA:C<sub>1</sub>C<sub>3</sub>pyrFSA = 10:90 mol%) and NaFSA-KFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA ionic liquids (NaFSA:KFSA:C<sub>1</sub>C<sub>3</sub>pyrFSA = 8:2:90, 5:5:90 and 0:10:90 mol%) were prepared by mixing each salt under magnetic stirring. Contents of impurities in the electrolytes such as metallic cations or halide anions were determined to be less than 10 ppm by ICP-AES and ion chromatography analysis. Electrochemical windows of NaFSA-KFSA [15] and NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA [21] systems have been previously measured as 5.2 V at 353 K. Water content of all electrolytes was determined to be less than 50 ppm by the Karl Fischer titration method.

HC (Carbotron P, Kureha Battery Materials Japan Co., Ltd.) and polyamide-imide binder were mixed in N-methyl-2-pyrrolidone (Kishida Chemical Co., Ltd., >99.5%) at a weight ratio of 96:4 using a dispersion mixer. The obtained slurry was coated onto an aluminum foil current collector and pressed by roller press. Loading density of HC was 4.7 (mg-HC) cm<sup>-2</sup>. Thickness of the obtained HC electrode was ca. 50  $\mu$ m.

Charge–discharge properties of the Na/HC cell were measured with a 2032 type two-electrode cell using a perfluoroalkoxy polymer gasket. The HC electrode was used as a positive (working) electrode. Sodium foil (Aldrich, >99.9%) was used for the negative (reference and counter) electrode. A microporous membrane (NPS050, Nippon Sheet Glass Co., Ltd., thickness: 50  $\mu$ m) was used as a separator. Charge–discharge tests were conducted at a constant charge current rate of 25 mA (g-HC)<sup>-1</sup> and discharge current rates of 25–1000 mA (g-HC)<sup>-1</sup> in the voltage region 0.005–1.200 V. Temperature of the cell was maintained at 363 K by a thermostatic oven during the charge–discharge tests.

## 3. Results and discussion

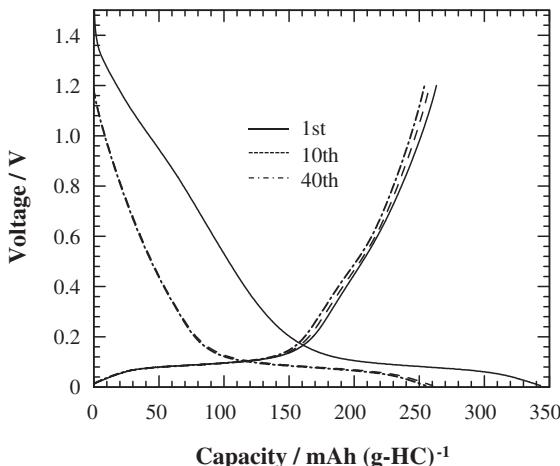
Fig. 2 indicates the charge–discharge curves of first, second, and third cycles for a Na/NaFSA-KFSA/HC cell at 363 K. Unfortunately, the cell showed poor charge–discharge properties; the capacity at first charge was 147 mAh (g-HC)<sup>-1</sup>, which is much smaller than the reported value of 250 mAh (g-HC)<sup>-1</sup> for NaClO<sub>4</sub>/PC at 298 K [19]. An even smaller capacity of 72 mAh (g-HC)<sup>-1</sup> was observed for the first



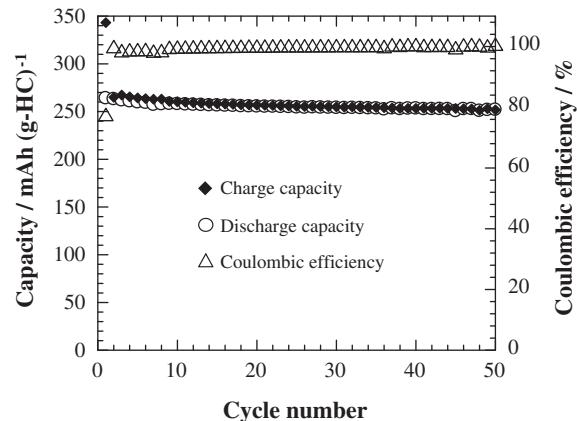
**Fig. 2.** Charge–discharge curves for a Na/NaFSA-KFSA/HC cell at 363 K. Charge–discharge rate: 50 mA (g-HC)<sup>-1</sup>; cut-off voltages: 0.005 and 1.200 V; cycle number: 1st, 2nd, and 3rd.

discharge. For the second cycle, charge and discharge capacities were largely decreased, displaying the values of 31 and 26 mAh (g-HC)<sup>-1</sup>, respectively. Since, Na<sup>+</sup> ions are known to be inserted/extracted into/from HC electrode, this result suggested that the HC electrode irreversibly reacted with the NaFSA-KFSA electrolyte, likely with K<sup>+</sup> ions. It was expected that an ionic liquid containing no potassium salt would give a reversible charge/discharge behavior.

Thus, a NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA (10:90 mol%) ionic liquid was used at the same temperature of 363 K. Fig. 3 shows the charge–discharge curves of a Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cell at the first (solid curve), 10th (dashed curve), and 40th cycle (dashed–dotted curve), respectively. At the first cycle, charge capacity was 343 mAh (g-HC)<sup>-1</sup>, and discharge capacity was 264 mAh (g-HC)<sup>-1</sup>. Fig. 4 shows the cycle properties of a Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cell. Although coulombic efficiency was 76.9% for the first cycle, it was drastically improved to 99% for the second cycle. The coulombic efficiency continuously improved as the charge–discharge cycle progressed, reaching 99.9% at the 37th cycle. The discharge capacity at the 50th cycle was 252 mAh (g-HC)<sup>-1</sup> corresponding to 95.5% of the first discharge capacity. These results confirm that Na<sup>+</sup> ions can be



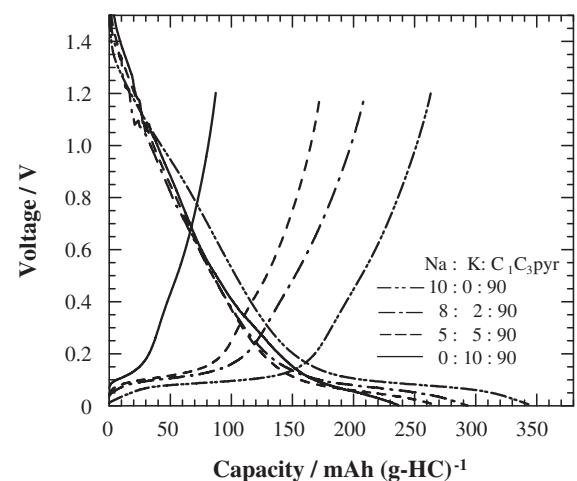
**Fig. 3.** Charge and discharge curves for a Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cell at 363 K. Charge–discharge rate: 50 mA (g-HC)<sup>-1</sup>; cut-off voltages: 0.005 and 1.200 V; cycle number: 1st, 10th, and 40th.



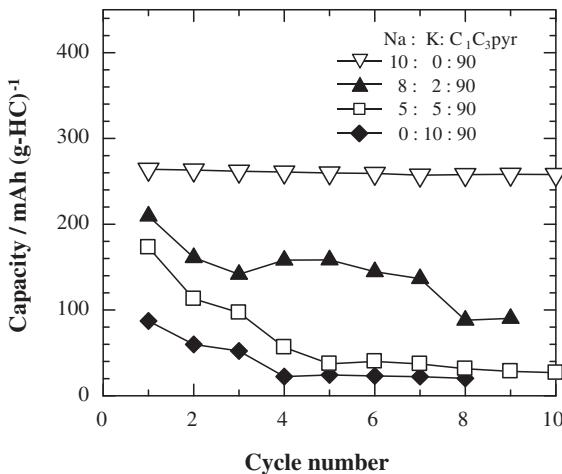
**Fig. 4.** Cycle dependence of charge capacity, discharge capacity, and coulombic efficiency for a Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cell at 363 K. Charge–discharge rate: 50 mA (g-HC)<sup>-1</sup>; cut-off voltages: 0.005 and 1.200 V.

practically inserted/extracted into/from the HC electrode reversibly in the NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA ionic liquid. It should be noted that only EC/DEC, PC, or EC/PC (EC: ethylene carbonate, DEC: diethyl carbonate, PC: propylene carbonate) systems have been previously reported to give a reversible charge–discharge behavior for HC [19,20]. Irreversible capacity for the initial few cycles (in total, 80 mAh (g-HC)<sup>-1</sup>) appears to be the cause of the formation of a solid electrolyte interphase (SEI), which was probably formed by decomposition of C<sub>1</sub>C<sub>3</sub>pyrFSA and/or NaFSA on the HC electrode surface. It is presumed that the SEI formation mainly occurs at a long sloping region at 1.3–0.2 V in the first charge curve in Fig. 3.

To investigate the influence of K<sup>+</sup> ions on Na<sup>+</sup> insertion, charge–discharge curves of the HC electrode were measured in ionic liquids with different compositions (NaFSA:KFSA:C<sub>1</sub>C<sub>3</sub>pyrFSA = 10:0:90, 8:2:90, 5:5:90, and 0:10:90 mol%) at 363 K. Fig. 5 shows the obtained curves at the first cycles. Here, the curves for 10:0:90 were observed to be the same as those shown in Fig. 3. The charge capacity decreased as the content of K<sup>+</sup> ion increased, i.e., 343, 285, 266, and 235 mAh (g-HC)<sup>-1</sup> for 10:0:90, 8:2:90, 5:5:90, and 0:10:90, respectively. More drastic differences were observed for the discharge capacities; the capacity decreased from 264 to 209, 173, and 87 mAh (g-HC)<sup>-1</sup>. These results indicate that the insertion



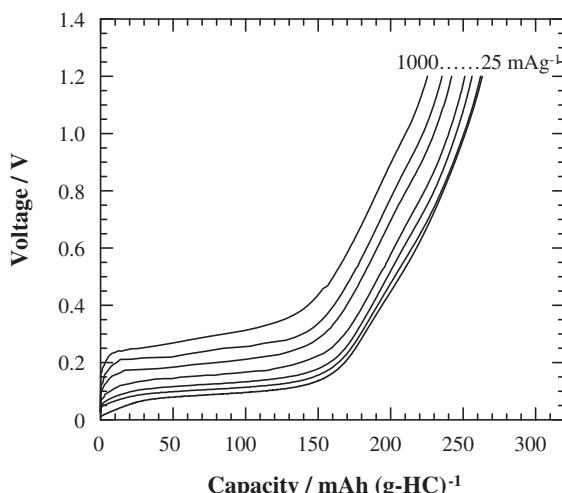
**Fig. 5.** Charge–discharge curves at the 1st cycle for Na/NaFSA-KFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cells (NaFSA:KFSA:C<sub>1</sub>C<sub>3</sub>pyrFSA = 10:0:90, 8:2:90, 5:5:90 and 0:10:90 mol%). Charge–discharge rate: 50 mA (g-HC)<sup>-1</sup>; operating temperature: 363 K; cut-off voltages: 0.005 and 1.200 V.



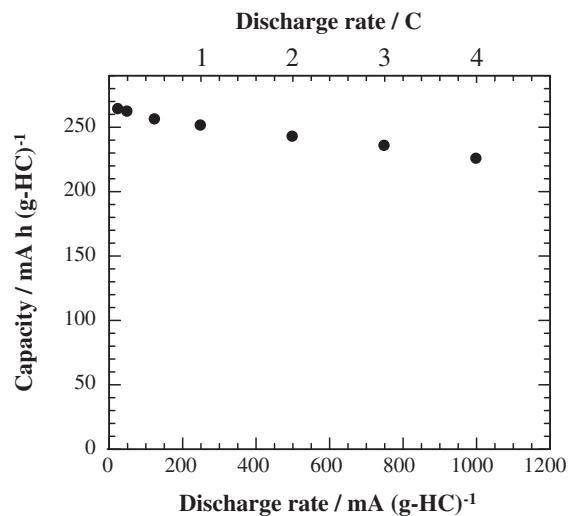
**Fig. 6.** Cycle dependence of discharge capacity for Na/NaFSA-KFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cells (NaFSA:KFSA:C<sub>1</sub>C<sub>3</sub>pyrFSA = 10:0:90, 8:2:90, 5:5:90 and 0:10:90 mol%) at 363 K. Charge–discharge rate: 50 mA (g-HC)<sup>-1</sup>; cut-off voltages: 0.005 and 1.200 V.

of K<sup>+</sup> ions into HC proceeds, and that once K<sup>+</sup> ions are inserted, they are more difficult to be extracted compared with Na<sup>+</sup> ions. The influence of K<sup>+</sup> ions was also clearly observed when the charge–discharge cycle was allowed to proceed. Fig. 6 shows the cycle dependence of discharge capacity for these cells. In contrast with the cell containing no K<sup>+</sup> ion, the increase in K<sup>+</sup> ions was found to exert a serious effect on the discharge capacity. It is obvious from these results that the existence of K<sup>+</sup> ions inhibits the reversible insertion/extraction of Na<sup>+</sup> ions into/from HC. One of the more conceivable explanations is as follows: when K<sup>+</sup> ions are inserted into HC, compounds with low crystallinity somehow structurally related to graphite intercalation compounds such as C<sub>8</sub>K and C<sub>12n</sub>K ( $n \geq 2$ ) [22,23] from which K<sup>+</sup> ions can be reversibly extracted may form. However, the presence of K<sup>+</sup> ions may change the nature of SEI film so that the incorporation of K<sup>+</sup> ions into the SEI film results in an increase of the electrical resistivity of film. The ratio of K<sup>+</sup> ion in the film increases due to the ion-exchange reaction as the charging and discharging cycle proceeds, resulting in a further increase of the resistivity and a decrease in the capacity.

Finally, the rate capability of the Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA (10:90 mol%)/HC cell was studied at 363 K. Fig. 7 shows discharge



**Fig. 7.** Discharge curves for a Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cell at 363 K. Charge rate: 25 mA (g-HC)<sup>-1</sup>; discharge rate: 25 (C/10), 50 (C/5), 125 (C/2), 250 (1C), 500 (2C), 750 (3C), and 1000 (4C) mA (g-HC)<sup>-1</sup>; cut-off voltage: 1.200 V.



**Fig. 8.** Rate dependence of discharge capacity for a Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cell at 363 K. Charge rate: 25 mA (g-HC)<sup>-1</sup>; discharge rate: 25 (C/10), 50 (C/5), 125 (C/2), 250 (1C), 500 (2C), 750 (3C), and 1000 (4C) mA (g-HC)<sup>-1</sup>; cut-off voltage: 1.200 V.

curves at currents of 25 (corresponding to ca. C/10), 50 (C/5), 125 (C/2), 250 (1C), 500 (2C), 750 (3C), and 1000 (4C) mA (g-HC)<sup>-1</sup>. The rate dependence of the discharge capacity is described in Fig. 8. All charging was conducted at a constant current of 25 mA (g-HC)<sup>-1</sup>. As can be seen from Fig. 7, the decrease in the discharge capacity was small even at high currents. At the discharge rate of 1000 mA (g-HC)<sup>-1</sup> (4C), a discharge capacity of 211 mAh (g-HC)<sup>-1</sup>, which corresponds to 80% of the capacity at 25 mA (g-HC)<sup>-1</sup> (C/10), was maintained. Discharge curves at higher rates exhibited a characteristic behavior corresponding to an increase in IR drop (voltage drop that caused by the DC resistance of the cell). This indicates that extraction of Na<sup>+</sup> ions from the HC nanostructure is not the rate-determining process during the discharge. Concerning the rate capability of the HC electrode in NaClO<sub>4</sub>/PC at room temperature (298 K) [20], it was reported that the discharge capacity decreased from >300 mAh (g-HC)<sup>-1</sup> at a rate of C/10 to 120 mAh (g-HC)<sup>-1</sup> at 2C. Thus, the HC electrode in NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA electrolyte at 363 K has a remarkably high rate capability.

#### 4. Conclusions

Charge–discharge properties of HC in a NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA ionic liquid have been investigated. The cycle test of a Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cell at 363 K revealed that the HC electrode has a reversible capacity of ca. 250 mAh (g-HC)<sup>-1</sup> in the NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA electrolyte, maintaining 95.5% of the first discharge capacity after 50 cycles with 99.9% coulombic efficiency. In contrast, a Na/HC cell with NaFSA-KFSA electrolyte showed poor reversibility. By using NaFSA-KFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA systems with various Na<sup>+</sup>/K<sup>+</sup> ratios, it was revealed that irreversible K<sup>+</sup> insertion inhibits the reversible Na<sup>+</sup> insertion into HC. Finally, it was demonstrated that a Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cell has an excellent rate capability. At a rate of 1000 mA (g-HC)<sup>-1</sup> (4C), a discharge capacity of 211 mAh (g-HC)<sup>-1</sup> was obtained, which corresponds to 80% of the capacity at 25 mA (g-HC)<sup>-1</sup> (C/10). Thus, it is concluded that this combination of HC electrode and NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA ionic liquid can provide a safe and high-rate negative electrode for sodium-ion batteries.

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## References

- [1] B.L. Ellis, L.F. Nazar, *Curr. Opin. Solid State Mater. Sci.* 16 (2012) 168–177.
- [2] M.D. Slater, D. Kim, E. Lee, C.S. Johnson, *Adv. Funct. Mater.* 23 (2013) 947–958.
- [3] Y. Kawabe, N. Yabuuchi, M. Kajiyama, N. Fukuhara, T. Inamasu, R. Okuyama, I. Nakai, S. Komaba, *Electrochemistry* 80 (2012) 80–84.
- [4] N. Yabuuchi, H. Yoshida, S. Komaba, *Electrochemistry* 80 (2012) 716–719.
- [5] S.-W. Kim, D.-H. Seo, X. Ma, G. Ceder, K. Kang, *Adv. Energy Mater.* 2 (2012) 710–721.
- [6] K. Chihara, A. Kitajou, I.D. Gocheva, S. Okada, J. Yamaki, *J. Power Sources* 227 (2013) 80–85.
- [7] N. Yabuuchi, M. Yano, H. Yoshida, S. Kuze, S. Komaba, *J. Electrochem. Soc.* 160 (2013) A3131–A3137.
- [8] N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada, S. Komaba, *Nat. Mater.* 11 (2012) 512–517.
- [9] J.L. Sudworth, *J. Power Sources* 11 (1984) 143–154.
- [10] T. Oshima, M. Kajita, A. Okuno, *Int. J. Appl. Ceram. Technol.* 1 (2004) 269–276.
- [11] J. Coetzer, *J. Power Sources* 18 (1986) 377–380.
- [12] C.-H. Dustmann, *J. Power Sources* 127 (2004) 85–92.
- [13] K. Kubota, T. Nohira, R. Hagiwara, *J. Chem. Eng. Data* 55 (2010) 3142–3146.
- [14] T. Nohira, T. Ishibashi, R. Hagiwara, *J. Power Sources* 205 (2012) 506–509.
- [15] A. Fukunaga, T. Nohira, Y. Kozawa, R. Hagiwara, S. Sakai, K. Nitta, S. Inazawa, *J. Power Sources* 209 (2012) 52–56.
- [16] C.Y. Chen, K. Matsumoto, T. Nohira, R. Hagiwara, A. Fukunaga, S. Sakai, K. Nitta, S. Inazawa, *J. Power Sources* 237 (2013) 52–57.
- [17] T. Yamamoto, T. Nohira, R. Hagiwara, A. Fukunaga, S. Sakai, K. Nitta, S. Inazawa, *J. Power Sources* 217 (2012) 479–484.
- [18] T. Yamamoto, T. Nohira, R. Hagiwara, A. Fukunaga, S. Sakai, K. Nitta, S. Inazawa, *J. Power Sources* 237 (2013) 98–103.
- [19] S. Komaba, W. Murata, T. Ishikawa, N. Yabuuchi, T. Ozeki, T. Nakayama, A. Ogata, K. Gotoh, K. Fujiwara, *Adv. Funct. Mater.* 21 (2011) 3859–3867.
- [20] A. Ponrouch, A.R. Gofñi, M.R. Palacín, *Electrochim. Commun.* 27 (2013) 85–88.
- [21] C. Ding, T. Nohira, K. Kuroda, R. Hagiwara, A. Fukunaga, S. Sakai, K. Nitta, S. Inazawa, *J. Power Sources* 238 (2013) 296–300.
- [22] J. Sangster, *J. Phase Equilib. Diffus.* 29 (2008) 73–83.
- [23] P.L. Walker, P.A. Thrower, *Chem. Phys. Carbon* 12 (1977) 1–37.